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## (54) IMPROVED ROOM-TEMPERATURE-CURABLE COMPOSITION

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a room-temp.-curable compsn. improved in depth curability and adhesiveness by incorporating a polymer having hydrolyzable silicon groups and at least one cure catalyst selected from among tin compds. into the same.

**SOLUTION:** This compsn. contains 100 pts.wt. polymer comprising a polymer (A) having hydrolyzable silicon groups represented by the formula:  $-\text{SiXaR13}-\text{a}$  and/or a polymer (B) having a polyoxyalkylene main chain, 0.01-10 pts.wt. at least one cure catalyst selected from among tin compds., and a filler, a plasticizer, etc. The tin compds. include a compd. (K) represented by the formula:  $\text{R22Sn(OZ)2}$ , a compd. (L) represented by the formula:  $[\text{R22Sn(OZ)2}]_n\text{O}$ , reaction product (M) of compd. K and a low-molecular compd. having a hydrolyzable silicon group, and a reaction product (N) of compd. L and a low-molecular compd. having a hydrolyzable silicon group. At least a part of polymer A is a polymer having a hydrolyzable silicon group of the formula wherein a is 3. In the formula, R1 is a monovalent org. group; R2 and Z are each a monovalent hydrocarbon group; X is a hydroxyl or hydrolyzable group; and a is 1-3.



or 11 in which a polymer (A) contains both polymers which has a hydrolytic silicon group whose a in a polymer in which a in a formula (1) has a hydrolytic silicon group which is 1 or 2, and a formula (1) is 3.

[Claim 14] The room-temperature-curing nature constituent according to claim 1, 2, 4, 5, 7, 8, 9, 10, or 11, whose polymer (A) is a polymer which has only a hydrolytic silicon group whose a in a formula (1) is 3 as a hydrolytic silicon group.

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[Translation done.]

## \* NOTICES \*

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1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. zett+ shows the word which can not be translated.

3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001] [Field of the Invention] This invention relates to the room-temperature-curing nature constituent which gives the hardened material over to result in an adhesive manifestation excelled [hardened material] in the adhesive property over short and various substrates.

[0002] [Description of the Prior Art] The method of making an end harden various kinds of polymers which have a hydroxylic silicon group, and using it for solvent, adhesives, etc. is known well, and is a useful method industrially. The polymer especially whose main chain is polyoxysiloxane among such polymers is liquefied at a room temperature, and when a hardened material holds pliability also at low temperature comparatively and uses for solvent, adhesives, etc. it is provided with the desirable characteristics.

[0003] As a constituent which uses such a polymer and it, with a molecular weight of 15000 or less silicon group content polymer, which two hydroxylic bases per silicon atom combine. Such a polymer has insufficient elongation and intensity of a hardened material, and in the case of the constituent hardened especially with the hygroscopic surface moisture in the air, there was a fault which is remarkably inferior in the hardenability of the depths. Although the polymer in which the amount of polymers and molecular weight distribution are very narrow, and its constituent are known for the compound which has the same end hydroxylic silicon group by JP-3-72527A, JP-4-232258A, etc. In this case, although the elongation, intensity, and hardenability of the hardened material have improved, it was not able to be said to make it harden promptly and obtain a hardened material especially, that that hardenability was still enough.

[0004] It is expected that, as for the silicon group which three hydroxylic bases combined with one silicon group, the hydroxylic rate becomes quick as compared with the silicon group which two hydroxylic bases combined, and the cure rate of the polymer which has such an end and becomes quick is a polymer which has a hydroxylic silicon group which three hydroxylic bases per silicon atom combine with JP-58-104118B or JP-58-10430B as such a polymer — a molecular weight — 6000 or less — the polymer of low molecular weight is indicated comparatively. Such a polymer was not enough in particular in respect of the inner drying property in low temperature, the elongation of a hardened material, or pliability, although the cure rate was quick to be sure. Especially these polymers had the fault that adhesive strength was low, when it was alone used for the use of an adhesive. [0005] In order to give room-temperature-curing nature to a polymer, especially a polysiloxane, what is called a curing catalyst, such as a curing catalyst, specific metal compounds, such as metal salts, carboxylic acid, tertiary or basic compound is known, and carboxylate of tin and other organotin compounds are especially common.

[0006] [Problem(s) to be Solved by the Invention] However, when it is made to harden using as a catalyst tetraalkyl organotin compounds known as a well-known example, such as dibutyltin diacetate and dibutyltin diacetate, a cure rate is not so-called can fully be satisfied, a part for a part especially from the surface of a cured body — the so-called cure rate of the depths is insufficient, and there was a problem also in an adhesive property with a substrate.

[0007] Although the method of using the reactant of an oxygenated tin compound and an ester

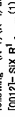
compound as a curing catalyst was also proposed by JP-1-58219B as a trial which cancels such a fault, the hardenability in low temperature was not enough.

[0008] In addition, the method of using a dialkyl tin bisacetate/isocyanate compound as a curing catalyst is also proposed by JP-81-141761A, and the hardenability in a room temperature and low temperature is also improved. However, combination with the organic polymer known conventionally proposed by the above-mentioned literature etc. was not enough as an internal hardenability compared with the speed of hardening of a surface layer.

[0009] A presentation which can improve depths hardenability and an adhesive property with a substrate without worsening the pliability and workability greatly was desired to the polymer which has a hydroxylic silicon group as mentioned above.

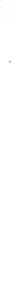
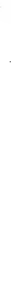
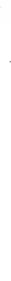
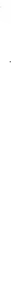
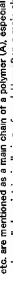
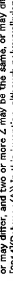
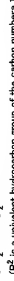
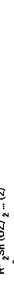
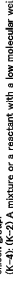
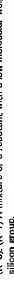
[Means for Solving the Problem] This invention relates to hardenability, especially a room-temperature-curing nature, a nature constituent by which time until it results in an adhesive manifestation was shortened using a specific curing catalyst.

[0011] It is a polymer which has a hydroxylic silicon group expressed with a following formula (1). Some or all of this polymer is a room-temperature-curing nature constituent which uses as an essential ingredient at least one sort of tin compounds (K) chosen from a polymer (A) which is a polymer which has a hydroxylic silicon group whose a of (1) is 3, and a group which consists of following — (K-1) (K-4) — as a curing catalyst.



(R<sup>1</sup>) is a univalent organic group substitution of the carbon numbers 1-20, or unsubstituted among a formula (1). X is a hydroxyl group or a hydroxyloxy basis, and a is 1, 2, or 3, however, when those R<sup>1</sup> may be the same, or may differ, when two or more R<sup>1</sup> exist, and two or more X exists, those X may be the same or may differ.

[0013] A tin compound (K): (K-1): A tin compound expressed with a following formula (2).



the molecular weights 8000-30000 as a raw material polyoxoalkylene polymer. Therefore, by [which manufactured using an alkali catalyst etc.] making many halogenated compounds, such as a methylene chloride, react to a polyoxoalkylene polymer of low molecular weight comparatively, it is possible to use a polyoxoalkylene polymer manufactured using a polyoxoalkylene polymer and a composite metal complex catalyst which are acquired by quantifying many.

[0019]Moreover — especially — a ratio of weight average molecular weight ( $M_w$ ) and a number average molecular weight ( $M_n$ ) — is being preferred that  $M_w/M_n$  uses 1.7 or less polyoxoalkylene polymer, and as for  $M_w/M_n$  it is still more preferred that it is 1.6 or less, and as for  $M_w/M_n$  it is preferred that it is especially 1.5 or less.

[0019]A polyoxoalkylene polymer (B) which has a hydrolytic silicon group of this invention is obtained by reacting a raw material polyoxoalkylene polymer (A) with a hydrolytic silicon compound, using such a compound as a raw material. When a raw material polyoxoalkylene polymer (B) obtained considering it as a raw material is subjected to that  $M_w/M_n$  of a raw material polyoxoalkylene polymer is small, elongation of a hardened material serves as high intensity greatly, and viscosity of a polymer becomes low, and what has a same steric modulus is excellent in workability. Especially, in the case of initiation of initiation. Especially in the case of initiation of initiation, it is preferred that what denaturalized and used an end of such an alkylene oxide polymer as a hydrolytic silicon group is the most preferred.

[0020]A complex which uses zinchexanoate or cobaltate as the main ingredients as a composite metal oxysilane complex is preferred, and ether and/or an alcohol compound are especially preferred. The presentation can use what is intrinsically indicated to JP46-272503 (B), in this case, as ether, ethyleneoxy dimethyl ether (glyme), diethylene glycol dimethyl ether (diglyme), etc. are preferred, and especially glyme is preferred from a point of handling at the time of manufacture of a complex. As alcohol, 1-butanol is preferred.

[0021]As for a functional group number of a raw material polyoxoalkylene polymer, two or more are preferred. As for especially a functional group number of a raw material polyoxoalkylene polymer, 2 or 3 is preferred to ensure pliability as the hardened material characteristic. As for especially a functional group number of a raw material polyoxoalkylene polymer, when acquiring a good adhesive property and hardenability, 3-8 are preferred. As a raw material polyoxoalkylene polymer, copolymer of a polyoxoethylene, polyoxopropylene, polyoxy butylene, polyoxy hexylene, polyoxy tetramethylene, and two or more sorts of cyclic ether is specifically mentioned.

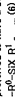
[0022]Especially a desirable raw material polyoxoalkylene polymer is the polyoxopropylene polyol of 2-6 valua, and are polyoxopropylene diol and polyoxopropylene triol especially. When using an allyl and polyoxopropylene monomer, can also be used.

[0023]The polyoxoalkylene polymer (B) is a hydrolytic silicon group expressed with an end or a side chain of 6 through a following formula (1).



(R<sup>1</sup>) is a univalent organic group substitution of the carbon numbers 1-20, or unsubstituted among a formula (1). X is a hydroxyl group or a hydrolytic basis, and a is 1, 2, or 3, however, when two or more R<sup>1</sup> exist, those R<sup>1</sup> may be the same, or may differ, and when two or more X exists, those X may be the same or may differ.

[0024]A hydrolytic silicon group expressed with a formula (1) is usually introduced into a raw material polyoxoalkylene polymer via an organic group. That is, as for a polyoxoalkylene polymer (B), it is preferred to have a basis expressed with a formula (2).



(A divalent organic group, R<sup>1</sup>, X, and a of R<sup>0</sup> are the same as that of the above among a formula (B)). [0025]R<sup>2</sup> in formula (1) (B) is a univalent organic group substitution of the carbon numbers 1-20, or unsubstituted. It is with a carbon number of eight or less alkyl group, a phenyl group, or a fluoro alkyl group preferably, and they are a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, a cyclohexyl group, a phenyl group, etc. especially preferably, when two or more R<sup>2</sup> exist,

those R<sup>2</sup> may be the same, or may differ.

[0026]As a hydrolytic basis in X, a halogen atom, an alkoxy group, an acyloxy group, an alkenyloxy group, a carbamoyl group, an amino group, an aminoxy group, a KETOXISIL mate group, etc. are mentioned, for example.

[0027]As for a carbon number of a hydrolytic basis which has a carbon atom among these, six or less are preferred, and four especially or less are preferred. As desirable X, a with a carbon number of four or less alkoxy group, an alkenyloxy group especially, a methoxy group, an ethoxy basis, a propoxy group, or a propenyl group can be illustrated, when two or more X exists, those X may be the same or may differ.

[0028]a is 1, 2, or 3. As for the number of hydrolytic silicon groups in one molecule of polymers, 1-8 are preferred, and 2-especially 6 are preferred.

[0029]Although a method in particular of introducing a hydrolytic silicon group to a raw material polyoxoalkylene polymer is not limited, it can be introduced, for example by (b) of the following — a method of (4).

[0030] (4) A method to which a hydrolytic compound expressed with it by a formula (7) after introducing an olefin group into an end of a polyoxoalkylene polymer which has a hydroxyl group is made to react.

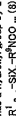


(R<sup>1</sup>, X, and a are the same as the above among a formula (7)).

[0031]A method of making a compound which has an unsaturation group and a functional group react to terminal hydroxyl groups of a polyoxoalkylene polymer which has a hydroxyl group, and combining it by ether bond, ester bond, a urethane bond, or carbonate combination as a method of introducing an olefin group, is mentioned. When polymerizing alkylene oxide, a method of introducing an olefin group into a side chain of a raw material polyoxoalkylene polymer can also be used by adding and carrying out copolymerization of the olefin group content epoxy compounds, such as allyl glycidyl ether.

[0032]When making a hydroxyl compound react, catalysts, such as allyl glycidyl ether, rhodium system catalyst, a cobalt system catalyst, a palladium system catalyst, and a nickel series catalyst, can be used. Platinum system catalysts, such as chloroplatinic acid, platinum chloride, a platinum chloride, and a platinum olefin complex, are preferred. As for a reaction to which a hydrolytic compound (4) is subjected, it is preferably preferred to carry out at temperature of 60-120 °C for several hours 30-150 °C.

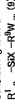
[0033] (4) A method to which a compound expressed with an end of a polyoxoalkylene polymer which has a hydroxyl group by a formula (8) is made to react.



(R<sup>1</sup>, X, and a are the same as the above among a formula (8)). R<sup>0</sup> is a divalent hydrocarbon group of the carbon numbers 1-17.

A publicly known urethane-lead catalyst may be used in the case of the above-mentioned reaction. As for the above-mentioned reaction, it is preferably preferred to carry out at temperature of 50-150 °C for several hours 20-200 °C.

[0034] (4) A method to which W basis of a silicon compound expressed with a formula (9) to this isooxanoate group is made to react after making polyisooxanoate compound, such as tolylene diisooxanoate, react to an end of a polyoxoalkylene polymer which has a hydroxyl group and considering it as an isooxanoate group end.



(R<sup>1</sup>, X, and a are the same as the above among a formula (9)). Active hydrogen containing group as which W is chosen from a hydroxyl group, a carboxyl group, a sulfinyl group, and an amino group (the 1st class or the 2nd class).

[0035] (4) A method to which the olefin group and a sulfinyl group of a silicon compound expressed with a formula (9) whose W is a sulfinyl group are made to react after introducing an olefin group into an end of a polyoxoalkylene polymer which has a hydroxyl group.

[0036]W as a silicon compound expressed with a formula (9) which is a sulfinyl group, 3-mercapto propylmethoxysilane, 3-mercapto propyldimethyl dimethoxysilane, 3-mercapto propyldimethyl dimethoxysilane, 3-mercapto propyldimethyl dimethoxysilane, etc. are mentioned.



and methacrylamide; Acrylonitrile, Cyano group content monomers, such as 2,4-dicyano butane-1,3-diol, vinyl ester system monomers, such as vinyl propionate, Butadiene, isoprene, Diene system monomers, such as chloroprene; Vinyl glycidyl ether, allyl glycidyl ether, glycidyl group content monomer [such as methacryloyl ether, glycidyl acrylate, and glycidyl methacrylate, ] and olefin other than these unsaturation ester species, a halogenated olefin, vinyl ether, etc. are mentioned.

[0055]A polymerization nature unsaturation group content monomer (C) may use only one sort, and may use two or more sorts together. When a cyano group content monomer, a glycidyl group content monomer, or a styrene monomer is used and acrylonitrile, glycidyl acrylate, glycidyl methacrylate, or styrene is used especially, show a further outstanding adhesive property and a mechanical physical property may be readily. It is desirable. When regarding rubber elasticity especially after hardening it is desirable.

[0056]A polymerization nature monomer which has a hydrolytic silicon group expressed with a formula (1) can be used as a polymerization nature unsaturation group content monomer (C). A compound expressed with a following formula (11) especially as a polymerization nature monomer which has such a hydrolytic silicon group is preferred.



(R<sup>1</sup>) is a univalent organic group which has a polymerization nature unsaturation group among a formula (11). R<sup>2</sup> is a univalent organic group substitution of the carbon numbers 1-20, or a substituted, Y is a hydroxyl group or a hydrolytic base, and s is 1, 2, or 3, however, when two or more R<sup>2</sup> exist, these R<sup>2</sup> may be the same, or may differ, and when two or more Y exists, these Y may be the same or may differ.

[0057]As a polymerization nature monomer which has a hydrolytic silicon group, a vinyl monomer which has a hydrolytic silicon group, an acrylic monomer which has a hydrolytic silicon group, etc. are mentioned. The following are specifically mentioned and 3-acryloyloxypropyl trimethoxysilane and especially 3-methacryloyloxypropyl trimethoxysilane are preferred.

[0058]Vinylmethyldimethoxysilane, vinylmethyldimethoxysilane, vinylmethyldichlorosilane, vinyltrimethoxysilane, vinyltrichlorosilane, vinyltriethoxysilane, vinyltriisopropoxysilane, 3-methacryloyloxypropyl trimethoxysilane, 3-methacryloyloxypropyl triethoxysilane, 3-methacryloyloxypropyl triisopropoxysilane, 3-methacryloyloxypropyl trimethoxysilane and 3-methacryloyloxypropyl triisopropoxysilane, and methacryloyloxypropyl silanes

[0059]A compound which has simultaneously a silicon atom which is a polysiloxane compound which has 2-30 silicon atoms other than this, for example, and was combined with a carbon-carbon double bond and a hydrolytic base can also be used as a polymerization nature monomer which has a hydrolytic silicon group.

[0060]A polymerization nature monomer which has the above-mentioned hydrolytic silicon group may use only one sort, and may use two or more sorts together. When using a polymerization nature monomer which has a hydrolytic silicon group, this monomer has that preferred of  $\text{ssr}$  for 0.01 - 20 weight sections among polymerization nature unsaturation group content monomer (C) 100 weight section.

[0061]As for a part or all of a polymerization nature unsaturation group content monomer (C), it is preferred that it is a monomer which has a hydrolytic silicon group which has a polymerization nature unsaturation group and is expressed with a glycidyl group and/or a formula (11).

[0062](Polymer composition) When a polyoxalkylene polymer (B) contains a polymer (D) further, a polymer composition which consists of a polyoxalkylene polymer (B) and a polymer (D) can be manufactured by a method of (4) shown below - (4).

[0063](4) How to mix a polymer (D) produced by polymerizing a polymerization nature unsaturation group content monomer (C) beforehand with a polyoxalkylene polymer (B).

(4) How to polymerize a polymerization nature unsaturation group content monomer (C) in a polyoxalkylene polymer (B).

(4) How to change an unsaturation group in a polymer group (F) which remains into a hydrolytic silicon group expressed with a formula (1) after polymerizing a polymerization nature unsaturation group content monomer (C) in a polyoxalkylene polymer group (F) containing an unsaturation group.

A converting method of a method to which a hydroxyl compound expressed with an unsaturation group by a formula (3) is made to react is preferred.

(\*) How to change a precursor into a polyoxalkylene polymer (B) after polymerizing a polymerization nature unsaturation group content monomer (C) in a precursor of a polyoxalkylene polymer (B).

(\*) How to mix with a polyoxalkylene polymer (B), rank second if needed, and distill off a solvent or a diluent after polymerizing a polymerization nature unsaturation group content monomer (C) under an extension of a solvent or a diluent.

[0064]A solvent can be suitably chosen according to a kind of polymerization nature unsaturation group content monomer (C). As a solvent, an unsaturation group content polyoxalkylene polymer (B) and a monomer (C) are preferred. A solvent (F) containing an unsaturation group can also be made to exist in a solvent or a diluent in the case of a polymerization nature unsaturation group content monomer (C).

[0065]Polymerization initiators, such as a radical generator, may be used, and it may be made to polymerize with radiation or heat in the case of a polymerization nature unsaturation group content monomer (C) polymerization, without using a polymerization initiator depending on the case. About a polymerization initiator, polymerization temperature, and polymerization time, it is the same as said (\*4) described.

[0066]When using a polymer (D) in this invention, it is preferred that the polyoxalkylene polymer used in polymer (D) is used in the range used as 100 / 1 - 1 / 300 at a weight ratio. It is preferred to be used in 100 / 1 - 1 / 100, further 100 / 1 - 1 / 10 especially in respect of workability etc.

[0067]It may be distributing uniformly in the shape of a particle in a polyoxalkylene polymer (B), or a polymer (D) may be dissolving uniformly again. When viscosity and workability of a constituent are taken into consideration, it is preferred to distribute uniformly in the shape of a particle.

[0068]In order to reveal an effect of this invention, a compound specific as a curing catalyst is indispensable. When not using such a curing catalyst, reaction velocity of crosslinking reaction of a hydrolytic silicon group will not become sufficient.

[0069]In this invention, at least one sort of tin compounds (X) chosen from a group which consists of following - (K-1) (X-1) to (X-7): A tin compound expressed with a following formula (2).

(X-1) compound expressed with a following formula (3)

(X-2) (K-1) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-3) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-4) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-5) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-6) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-7) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-8) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-9) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-10) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-11) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-12) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-13) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-14) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-15) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-16) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-17) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-18) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.

(X-19) (K-2) A mixture of a reactant with a low molecular weight compound (L) which has a hydrolytic silicon group.







[0111] Drying oil represented by tung oil, linseed oil, etc. as such an air-oxidation hardenable compound, an acryloyl polymer which denaturalized with various allyl resins produced by denaturalizing this compound, and drying oil. Various denaturation things (nellar-tized denaturation, boiled oil denaturation, etc.) of these system polymers, such as a polymer of silicone resin, polybutadiene, and diene of the carbon numbers 6-8 and a copolymer, and also this polymer, or a copolymer, etc. are mentioned. As a photosensitized compound, polyfunctional acrylates is usually used in addition, organo colors, such as inorganic pigments, such as iron oxide, chrome oxide, and titanium oxide, and copper phthalocyanine blue, and phthalocyanine Green, are mentioned to paint. [0112] A room-temperature-curing nature constituting of the invention is suitable for a use as which it can be used for sealant, water blocking material, adhesives, a coating agent, etc., and dynamic factory failure to sufficient cohesive force and adhesion of especially the hardened material itself is obtained. [0113]

[Example 1] The example and comparative example which produced the hardened material are shown below using the polymer (P1-P11, P13-P23) manufactured in the examples 1-11, 13-23 of manufacture. A part shows a weight section. In the examples 1-12 of manufacture, a hydroxyl value conversion molecular weight shows the molecular weight converted from the hydroxyl value of the polyoxyalkylene polymer which has a hydroxyl group which is a raw material.  $M_n$  is the value measured by the gel permeation chromatograph using a tetrahydrofuran as a solvent. The analytical curve was prepared using polyoxyalkylene glycol. In the examples 14-23 of manufacture, the molecular weight was measured by the gel permeation chromatograph, using a tetrahydrofuran as a solvent. The analytical curve was prepared using polystyrene.

[0114] (Example 1 of manufacture) Glycerol was used as the initiator and the bottom propylene oxide of existence of a zincchrysocollate glyme complex compound catalyst was made to react. The methanol solution of sodium methoxide was added to polyoxypropylene triol of hydroxyl value conversion molecular weight: 17000 and  $M_n/M_w=1.3$ , scale less pressing-down method was distilled off and the terminal hydroxyl groups of polyoxypropylene triol was changed into sodium alcoholate. Next, the allyl chloride was made to react. The unreacted allyl chloride was removed and refined and the allyl group and polyoxypropylene oxide was obtained (let this be the polymer U1). When the hydroxyl group which remains was analyzed by the measuring method of the hydroxyl value, they were 0.01 millimole/g. The trimethoxysilane which is a hydroxyl compound was made to react under existence of a platinum catalyst to the polymer U1, and the polymer P1 which has an average of two trimethoxysilyl groups at the end was obtained.

[0115] (Example 2 of manufacture) The polyoxypropylene glycol of hydroxyl value conversion molecular weight [which used propylene glycol as the initiator, made the bottom propylene oxide of existence of a zincchrysocollate glyme complex compound catalyst react, and was obtained] 17000, and  $M_n/M_w=1.3$  is used. The polyoxypropylene oxide which has an allyl group at the end by the same method as the example 1 of manufacture was obtained (the hydroxyl groups which remain are 0.01 millimole/g). The trimethoxysilane which is a hydroxyl compound was made to react under existence of a platinum catalyst to this reactant, and the polymer P2 which has an average of 1.3 trimethoxysilyl groups at the end was obtained.

[0116] (Example 3 of manufacture) Polyoxypropylene hexanol of hydroxyl value conversion molecular weight [which used sorbitol as the initiator, made the bottom propylene oxide of existence of a zincchrysocollate glyme complex compound catalyst react, and was obtained] 15000, and  $M_n/M_w=1.3$  is used. The polyoxypropylene oxide which has an allyl group at the end by the same method as the example 1 of manufacture was obtained (the hydroxyl groups which remain are 0.01 millimole/g). The trimethoxysilane which is a hydroxyl compound was made to react under existence of a platinum catalyst to this reactant, and the polymer P3 which has an average of 3.9 trimethoxysilyl groups at the end was obtained.

[0117] (Example 4 of manufacture) The mixture which made the molar ratio methyl dimethoxysilane and trimethoxysilane which are hydroxyl compounds, and was mixed in proportion of 30 to 70 is made to react under existence of a platinum catalyst to the polymer U1 manufactured in the example 1 of manufacture. The polymer P4 which has simultaneously an average of 0.05 methyl dimethoxysilyl group and an average of 1.4 trimethoxysilyl groups at the end was obtained.

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[0118] (Example 5 of manufacture) 3-mercaptopropyltrimethoxysilane which is a silyl compound to the polymer U1 manufactured in the example 1 of manufacture, it was made to react with the 2,2'-azobis (2-methylpropanitrile) which is a polymerization initiator, and the polymer P5 which has an average of two trimethoxysilyl groups at the end was obtained.

[0119] (Example 6 of manufacture) It refined after polymerizing propylene oxide using the zincchrysocollate catalyst by heating glycerol as the initiator and obtaining polyoxypropylene triol of hydroxyl value conversion molecular weight: 17000 and  $M_n/M_w=1.3$ .

Isocyanate propyltrimethoxysilane was added to this, the urethane-ized reaction was performed, the end was changed into the trimethoxysilyl group, and the polymer P6 of the molecular weight: 18000 which has an average of two trimethoxysilyl groups at the end was obtained.

[0120] (Example 7 of manufacture) To the polymer U1 manufactured in the example 1 of manufacture, methyl dimethoxysilane which is a hydroxyl compound was made to react under existence of a platinum catalyst, and the polymer P7 which has an average of two methyl dimethoxysilyl groups at the end was obtained.

[0121] (Example 8 of manufacture) The polyoxypropylene glycol of hydroxyl value conversion molecular weight [which used propylene glycol as the initiator, made the bottom propylene oxide of existence of a zincchrysocollate glyme complex compound catalyst react, and was obtained] 7000, and  $M_n/M_w=1.2$  is used. The polyoxypropylene oxide which has an allyl group at the end by the same method as the example 1 of manufacture was obtained (the hydroxyl groups which remain are 0.01 millimole/g). Methyl dimethoxysilane which is a hydroxyl compound was made to react under existence of a platinum catalyst to this reactant, and the polymer P8 which has an average of 1.3 trimethoxysilyl groups at the end was obtained.

[0122] (Example 9 of manufacture) The polyoxypropylene glycol of hydroxyl value conversion molecular weight [which used propylene glycol as the initiator, made the bottom propylene oxide of existence of a zincchrysocollate glyme complex compound catalyst react, and was obtained] 7000, and  $M_n/M_w=1.2$  is used. The polyoxypropylene oxide which has an allyl group at the end by the same method as the example 1 of manufacture was obtained (the hydroxyl groups which remain are 0.01 millimole/g). The trimethoxysilane which is a hydroxyl compound was made to react under existence of a platinum catalyst to this reactant, and the polymer P9 which has an average of 1.3 trimethoxysilyl groups at the end was obtained.

[0123] (Example 10 of manufacture) The methanol solution of sodium methoxide was added to polyoxypropylene triol of the hydroxyl value conversion molecular weight: 3000 obtained using the potassium hydroxide catalyst, scale less pressing-down method was distilled off, and terminal hydroxyl groups were changed into sodium alcoholate. Next, the allyl chloride was made to react continuously, after making it react to chloromethane and performing polymers quantification. The unreacted allyl chloride was removed and refined and the polyoxypropylene oxide ( $M_n/M_w=1.9$ ) which has an allyl group at the end was obtained (the hydroxyl groups which remain are 0.01 millimole/g). The polymer P10 of the molecular weight: 7000 which makes the trimethoxysilane which is a hydroxyl compound react to this under existence of a platinum catalyst, and has an average of 1.3 trimethoxysilyl groups at the end was obtained.

[0124] (Example 11 of manufacture) Polyoxypropylene diol of hydroxyl value conversion molecular weight [which was obtained using the potassium hydroxide catalyst] 6000 and  $M_n/M_w=1.9$  is used. The polyoxypropylene oxide which has an allyl group at the end by the same method as the example 1 of manufacture was obtained (the hydroxyl groups which remain are 0.01 millimole/g). The trimethoxysilane which is a hydroxyl compound was made to react to this under existence of a platinum catalyst, and the polymer P11 which has an average of 1.3 trimethoxysilyl groups at the end was obtained.

[0125] (Example 12 of manufacture) Add 49.8 g (0.2 mol) of dibutyltin oxide to toluene 1500<sup>cm3</sup> in glass reactors, and 13.0 g (0.1 mol) of 2-ethylhexanol is added. It was made to react removing the water which carries out azeotropy to bottom toluene of heating, churning until the water of the amount of theories finishes distilling off. 10.0 g (0.1 mol) of acetylsalicylates are added after that, and it was made to react removing the water which carries out azeotropy to toluene further until the water of the amount of theories finishes distilling off. It filtered in order to remove a little sediments, and it distilled off under decompression of toluene further, and the light yellow fluid compound (Q) was

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